

# ***U.S. PATENT APPLICATION***

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***Invention:*** ENVIRONMENTALLY-FRIENDLY FIBERLINE FOR PRODUCING  
BLEACHED CHEMICAL PULP

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## ***SPECIFICATION***

**ENVIRONMENTALLY-FRIENDLY FIBERLINE FOR PRODUCING BLEACHED  
CHEMICAL PULP**

**CROSS-REFERENCE TO RELATED APPLICATION**

This application is based upon provisional application serial no. 60/167,537 filed  
5 December 2, 1999, the disclosure of which is hereby incorporated by reference herein.

**BACKGROUND AND SUMMARY OF THE INVENTION**

Increased concerns about the impact of the chemical pulping and bleaching 5  
process has resulted in attempts to, among other things, limit the use of chlorine-containing  
compounds in the processing of cellulose material to make cellulose pulp for the  
10 manufacture of paper. This is especially true in the bleaching of cellulose pulp in which  
attempts have been made to replace the use of oxidative chlorine-containing compounds  
with more environmentally benign oxygen-containing compounds such as oxygen,  
peroxide, and ozone. For example, the recently proposed legislation enacted by the U.S.  
Environmental Protection Agency (EPA), referred to as the "Cluster Rules", limits the  
15 release of certain chemical compounds associated with chlorine-containing bleaching  
agents in both the gaseous and liquid effluents leaving a pulp mill.

As a result, various Totally-Chlorine-Free (TCF) or Elemental-Chlorine Free (ECF)  
bleaching sequences have been proposed and some are in commercial operation. For  
example, in TCF bleaching, no chlorine-containing chemicals, in particular no chlorine ( $\text{Cl}_2$ ,  
20 or simply designated "C") or chlorine dioxide ( $\text{ClO}_2$ , or simply "D"), are used in the  
bleaching of pulp. In ECF bleaching, elemental chlorine is eliminated from the bleach plant  
in favor of more environmentally benign chlorine dioxide. Typical, TCF bleaching  
sequences include the use of oxygen gas ( $\text{O}_2$ , or simply "O"), ozone gas ( $\text{O}_3$ , or simply "Z"),  
and hydrogen peroxide ( $\text{H}_2\text{O}_2$ , or simply "P"), among others, while ECF bleaching  
25 sequences also include the use of chlorine dioxide (D).

Also, TOF and ECF bleaching sequences are susceptible to the damaging effects of  
the presence of dissolved metal ions such as dissolved iron (Fe), copper (Cu), and

manganese (Mn), among others. Not only can these "non-process elements" become concentrated in the "closed-cycle" bleaching effluents of the TCF and ECF bleaching sequences, but these metals, especially, Mn, are recognized as detrimental to the effective treatment of pulp with non-chlorine bleaching agents, most notably, hydrogen peroxide. As a result, it is also desirable to limit the presence of such dissolved metals in the pulp and liquid treatment streams in and around the pulp mill. Typical treatments used to minimize the presence of these metals include acid washing and chelate treatment, for example, using conventional chelating agents EDTA and DPTA, among others.

There is also interest in reducing the release of gases containing malodorous sulfur-containing compounds, such as hydrogen sulfide ( $H_2S$ ), methyl mercaptan ( $CH_3SH$ ), dimethyl sulfide ( $CH_3SCH_3$ ), and dimethyl disulfide ( $CH_3S_2CH_3$ ), among others, (collectively referred to as Total Reduced Sulfur (TRS) gases) from the gases released from pulp mills. These sulfur-containing gases are generally associated with the "sulfate" or "kraft" pulping process in which the predominant pulping chemicals are sodium sulfide ( $Na_2S$ ) and sodium hydroxide ( $NaOH$ ). One alternative to the kraft process is the "soda" process in which the active pulping chemical is limited to  $NaOH$  alone, that is, no sulfur-containing chemicals are used in the pulping process (though some sulfur may be introduced via the wood supply or through oil burned in the mill's boilers).

However, the soda process is recognized as producing a somewhat inferior product than the kraft process. That is, the soda process typically produces a pulp having lower yield and strength properties than the kraft process. To address this limitation of the soda process, attempts have been made to introduce strength or yield-enhancing additives to the soda process to improve the quality of the pulp produced. Most notably, anthraquinone (AQ) has been introduced with limited success to provide what has been known as the "soda-AQ" process.

One recently recognized effect of the treatment of cellulose material, that is, wood chips, with AQ is the undesirable "yellowing" of the resulting pulp from the AQ treatment. That is, pulps produced in the presence of AQ have exhibited a yellow or orange color which, especially for fully-bleached pulps, is undesirable. It has been recognized according to the invention that an effective method of reducing or eliminating this undesirable

discoloration is by treating the AQ-treated pulp with an oxidizing agent, for example, air, oxygen gas, peroxide, or most preferably ozone gas.

In addition, it has also been recently recognized that the processes described in U.S. patents 5,489,363; 5,536,366; 5,547,012; 5,575,890; 5,620,562; 5,662,775; and  
 5 others, and marketed under the trademark LO-SOLIDS (by Andritz-Ahlstrom Inc. of Glens Falls, NY, produces cellulose pulp having improved strength properties (manifest as an increase in viscosity) compared to pulps produced by conventional methods, especially in comparison to the soda process. In addition, the use of ozone has also been known to negatively affect pulp viscosity. Thus, the embodiment of the present invention employing LO-SOLIDS cooking methods and AQ treatment can offset the negative effects of soda cooking and ozone bleaching on the strength and quality of the pulp produced.

Thus, by eliminating or minimizing the presence of sulfur in the pulping process and chlorine in the bleaching process, while maintaining or improving the quality (that is, the strength and yield of the bleached pulp produced) the present invention provides an environmentally-friendly and commercially viable process for producing fully-bleached cellulose pulp from comminuted cellulosic fibrous material.

One embodiment of the present invention comprises a method of treating a slurry of comminuted cellulosic fibrous material to produce a bleached chemical pulp, comprising or consisting of the following: a) treating the material in a first stage with a gas containing  
 20 ozone; and b) treating the material in a second stage with a liquid containing chlorine dioxide; wherein between a) and b) the material is treated with an alkaline liquid to raise the pH of the material prior to b) and wherein no washing is performed between a) and b). Preferably between a) and b) the pH of the material is raised to at least about 6.0, preferably, at least 7.0. The present invention may be expressed by the notation (ZEND),  
 25 where Z represents an acidic treatment with an ozone containing gas, EN is an alkaline neutralization treatment, and D is an alkaline treatment with chlorine dioxide; again, no washing is performed between these treatments.

According to the present invention, the alkaline neutralization treatment, EN, performs at least two recognized functions. First, the increase in alkalinity to an  
 30 approximately neutral pH, that is, to a pH of between about 6 and 8, preferably, about 7, solubilizes the products of reaction from the prior Z stage. For example, the lignin-

containing compounds oxidized in the Z stage are kept in solution by the addition of alkali to the ozonated pulp. Where in conventional alkaline extraction stages, these solubilized compounds are removed in a subsequent washing of the pulp prior to further treatment, according to the present invention, no washing (the term "washing" also includes pressing and thickening) is necessary, and the solubilized lignin-containing compounds are passed to the following alkaline chlorine dioxide treatment. The lignin-containing compounds can be subsequently removed in a washing stage following the chlorine dioxide stage.

Secondly, the introduction of alkali in the neutralization stage also increases the pH of the pulp to a range that is more compatible with the subsequent alkaline D stage. It is known in the art that it is preferable to initiate the chlorine dioxide treatment in an alkaline state, however, during chlorine dioxide treatment the pH typically drops as acids are formed. In effect, the alkali introduced in the EN stage offsets the amount of alkali that needs be added to adjust the pH for the D stage. According to the present invention, not only is a more effective treatment of the pulp obtained, that is, a more effective removal of chromophoric compounds, but also the need for an expensive washing device is obviated.

In a preferred embodiment, prior to a) the material is treated in an alkaline chemical pulping process, preferably an essentially sulfur-free pulping process, such as a soda pulping process. This alkaline pulping process also preferably includes treatment with a strength or yield enhancing additive such as anthraquinone or polysulfide, or their equivalents or derivatives. The preferred additive is anthraquinone, AQ, because AQ has been shown to off-set the reduced yield characterized by the soda process, in comparison to the kraft process. In addition, the alkaline pulping process preferably includes a bulk delignification stage and the process includes at least one stage prior to or during the bulk delignification stage in which a liquid containing a first level of dissolved organic material is removed from the material and replaced with a second liquid having a lower (e.g. at least 50% lower) level of dissolved organic material, as described in the aforementioned patents (the disclosures of which are hereby incorporated by reference herein).

Also, the treatment a) is preferably preceded by, c), treating the material with a liquid containing chlorine dioxide followed by d) treating the material with an alkaline liquid.

Specifically, it is preferred that the treatment c) is a treatment with chlorine dioxide (D) and d) is a treatment with an alkaline liquid to solubilize and extract (E) the oxidized products

produced in c). The alkaline liquid in d) is typically sodium hydroxide. That is, one preferred embodiment is the bleaching sequence D-E-(ZEND), in which washing is performed before, between, and after the first D and first E stages (as indicated by the hyphens in the bleaching sequence designation) and no washing is performed between the Z, EN and D stages (as indicated by enclosing those symbols within parenthesis without hyphens between them in the bleaching sequence designation). The first treatment with the alkaline liquid (E) may also include the presence of oxygen, a peroxide, or both. That is, this stage may also be an E<sub>O</sub>, E<sub>P</sub> or E<sub>OP</sub> stage.

Another embodiment of the present invention includes a method for producing bleached chemical pulp from comminuted cellulosic fibrous material comprising the following: a) treating the material in a chemical pulping process in the presence of chemical additive to produce a chemical pulp containing at least some of the additive; b) treating the chemical pulp with at least one elemental chlorine-free bleaching agent to produce a bleached chemical pulp having at least some discoloration due to the presence of the chemical additive; and c) treating the bleached pulp with at least one oxidizing agent to remove the discoloration produced by the presence of the chemical additive. In a preferred embodiment the chemical additive used in the pulping process of a) is anthraquinone or its equivalents or derivatives. The discoloration of the pulp due to the presence of the additive, typically AQ, is characterized by a yellowish or orange tinge to the pulp.

The at least one bleaching agent used in the treatment b) is preferably one or more of the following bleaching agents: oxygen, chlorine dioxide, sodium hydroxide, ozone, hydrogen peroxide, but most preferably comprises at least chlorine dioxide. The oxidizing agent used in c) is typically air, ozone, oxygen, or peroxide, but is preferably an ozone-containing gas.

According to another aspect of the invention there is provided a method of ECF treatment of comminuted cellulosic fibrous material comprising the sequence soda/AQ cooking, and then one of D-E<sub>P</sub>-(ZEND), or D-E<sub>O</sub>-(ZEND), or D-E<sub>OP</sub>-(ZEND). The pulp so produced has a brightness of at least 89 or 90% ISO, and a viscosity of over 21 or 22 cP.

According to the present invention, an environmentally-friendly and commercially viable process for producing fully-bleached cellulose pulp from comminuted cellulosic fibrous material is provided. While the invention has been described in connection with

what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiment, but on the contrary, is intended to cover various modifications and equivalent arrangements and methods and to be limited only by the prior art.

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### **BRIEF DESCRIPTION OF THE DRAWINGS**

FIGURE 1 is a schematic illustration of a complete fiberline of one exemplary embodiment according to the present invention;

FIGURE 2 is a schematic detailed illustration of a subsystem of the fiberline of FIGURE 1;

FIGURE 3 is a graph of viscosity versus brightness showing the properties of pulp produced according to the present invention compared to various prior art processes; and

FIGURE 4 is a graph like that of FIGURE 3 only plotting brightness versus chlorine dioxide consumption.

### **DETAILED DESCRIPTION OF THE DRAWINGS**

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FIGURE 1 is a schematic illustration of a typical complete environmentally-friendly and commercially viable fiberline, or cellulose material treatment system, 10, according to the present invention. Comminuted cellulosic fibrous material 11, typically hardwood or softwood chips, though any other form of comminuted cellulosic fibrous material may be treated according to the invention, is introduced to a digester 12. Though the present invention is most amenable to treatment in a continuous digester, digester 12 may also be a batch digester. According to the preferred embodiment of this invention, the pulping process is preferably a sulfur-free alkaline cooking process, preferably a soda/AQ process. Caustic soda, or sodium hydroxide, is introduced to digester 12 along with the chips via conduit 13 and AQ, or its equivalent or derivative, is introduced via conduit 14. The treated pulp is discharged from the digester into conduit 15.

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As is conventional, the cooked pulp is typically treated in one or more brownstock washers 16 to recover some of the cooking chemical and to clean the pulp slurry prior to further treatment. The cleaned pulp is passed via conduit 17 to optional alkaline oxygen

delignification 18 and post oxygen delignification washing 20 via conduit 19. The oxygen treatment is preferably performed in one or two stages at medium consistency, that is, at a pulp consistency between about 8 and 18%. The washed pulp, with or without oxygen treatment, is passed to further treatment via conduit 21.

5           Conduit 21 introduces the pulp to the first formal bleaching stage 22, which is preferably an alkaline chlorine dioxide treatment, DO. This treatment 22 may be performed at medium consistency or at low consistency, that is, at a pulp consistency between 0.5 to 18%, preferably between about 2-8% (and all other specific narrower ranges within the broad range). The treated pulp is then passed via conduit 23 to washer 24. Washer 24 may be any conventional washer, such as a vacuum drum washer, a wash press, a diffusion washer, or a belt washer. Washing in one or more washers 24 may be performed at low or medium consistency as is conventional.

10           The washed pulp is passed via conduit 25 to alkaline extraction stage (E) 26 (which may be an E<sub>O</sub>, E<sub>P</sub>, or E<sub>OP</sub> stage) which is a conventional alkaline treatment with sodium hydroxide which solubilizes the products of reaction of stage 22. The pulp from extraction stage 26 is forwarded to another conventional washing stage 28, similar to stage 24, via conduit 27. The washed pulp is forwarded to the ozone treatment stage 30 via conduit 29.

15           Treatment stages 30, 34 and 38 constitute the broadest embodiment of the present invention. In stage 29 the pulp, preferably at medium consistency (e.g. about 6-18%),  
20           though it may be at low (.5-5%) or high (over 18%) consistency, is treated with an ozone containing gas introduced via conduit 31. This ozone-containing gas typically is generated and introduced using of a carrier gas, for example, oxygen or air, at a concentration greater than 5%, typically between about 5 and 15%. Though this ozone containing gas is typically produced on-site, it may be supplied from an external source. The ozone-containing gas is  
25           typically provided in a pressurized state to a high-intensity mixer, for example, to an AMZ mixer supplied by Andritz-Ahlstrom Inc. of Glens Falls, NY. The treatment in stage 30 is typically in an acidic environment, typically, at a pH less than 5, preferably a pH between about 2 and 3. After ozone treatment 30, the treated pulp is passed to alkaline treatment 34 via conduit 32. If desired, due to the relatively large volumes of gas introduced to the pulp  
30           via conduit 31, some de-gassing 33 may be performed after treatment 30 and before treatment 34, but no washing (which term includes pressing and thickening).



Alkaline treatment 34 is typically a relatively short exposure of the ozonated pulp to alkali, typically NaOH, introduced via conduit 35. The retention time in treatment 34 is typically less than 30 minutes, preferably less than 15 minutes. As discussed above, the treatment 34, among other things, neutralizes the acidic pulp discharged from treatment 30 that the products of the reaction in treatment 30 are maintained in a solubilized state. The pH in stage 34 is typically between about 6 and 8, preferably about 7. However, unlike the prior art, these solubilized compounds are not washed out of the pulp after treatment in 34 but are passed directly to alkaline treatment 38, D1, via conduit 36. As before, some degassing 37 may be performed between stages 34 and 38, if necessary. The unwashed pulp introduced to treatment 38 via conduit 36 is treated with chlorine dioxide, ClO<sub>2</sub>. The chlorine dioxide is introduced to the pulp via conduit 39 and a mixer (see mixer 59 in FIGURE 2), for example, a conventional high-intensity mixer.

The treated pulp is then passed via conduit 40 to conventional washing in stage 41 and then, if desired, to further treatment via conduit 42, for example, to further elemental chlorine-free bleaching stages (so that the entire treatment of the pulp is ECF), to storage, to stock preparation before a paper machine, if the mill is an integrated paper mill, or to a pulp drier, if the mill is a market pulp mill.

FIGURE 2 illustrates a specific embodiment of stages 30, 34 and 38 shown in FIGURE 1. Structures in FIGURE 2 that are similar to those in FIGURE 1 are identified with similar reference numbers, but in FIGURE 2 the reference numbers are 10 prefaced by the numeral "1". For example, the conduit 129 in FIGURE 2 is essentially the same as conduit 29 in FIGURE 1.

Pulp from washer 28 in FIGURE 1 is introduced to treatment 130 via conduit 129 in FIGURE 2. Treatment 130 is preferably performed in a mixer 50 to which an ozone-containing gas, typically ozone in an oxygen carrier gas, is introduced via conduit 131. The ozone treatment step is typically performed at a temperature less than 100°C, for example, at a temperature between about 20 and 70°C, depending upon the energy balance of the system. The acidic ozone treatment 130 is typically performed at a pH less than 5, preferably, a pH between about 2 and 3. However, the ozone treatment 130 may be performed at a pH of greater than 5, even greater than 7, if ozone decomposition and cellulose damage can be avoided or minimized at such higher pH values.

The ozonated pulp is discharged from the mixer 50 to conduit 132. Since the reaction of the ozone with the pulp is very rapid, for example, the reaction may typically take less than 30 seconds, no retention vessel is normally necessary after the mixer 50 and the ozonated pulp may be passed directly to the alkaline neutralization stage 134. However, if desired, a retention vessel 51 may be used after the mixer 50. Though not shown in FIGURE 2, the pulp may be de-gassed after mixer 50 and before stage 134.

The ozone-treated pulp is introduced to alkaline neutralization stage 134 via conduit 132. Treatment 134 is effected by the introduction of alkali, preferably NaOH via conduit 135, to mixer 52, again, preferably a high-intensity mixer. Again, due to the rapid reaction of ozone with the pulp, especially at medium consistencies, the alkali in conduit 135 may also be introduced directly to mixer 150 via conduits 62 and 131. In a specific embodiment of this invention, it may even be possible to eliminate the mixer 52 and introduce both the ozone-containing gas and the alkali to mixer 50.

Assuming the embodiment shown with two mixers, 50 and 52, after introducing alkali to the pulp via mixer 52 the pulp is discharged to conduit 53. The pulp is retained in this alkaline state, typically at a temperature of between about 20 and 70°C, preferably at a temperature of between about 50 and 70°C, for at least about 15 minutes, preferably at least between about 30 minutes and about 60 minutes. This retention can be effected in a conventional retention vessel (not shown) or in a pump feed chute 54. In a preferred embodiment, at least some de-gassing 137 of the pulp is effected as the pulp is introduced to feed chute 54, in any suitable conventional manner. The pulp may also be de-gassed in a specially-designed rotary de-gassing device if desired.

From the feed chute 54, or retention vessel (not shown), the pulp is pumped to chlorine dioxide treatment 138 via pump 55. The pump 55 may be a de-gassing-type pump from which gas is removed via conduit 56. The pump 55 passes the pulp through conduit 57 to mixer 59, again, preferably a high-intensity mixer, to which chlorine dioxide is introduced via conduit 139. If desired, the pulp in conduit 57 may be heated by introducing steam via conduit 58. The pH of the pulp discharged to vessel 61 is typically at least 5, preferably at least 6. Additional alkali may also be added to the pulp, for example, via conduit 63. The chlorine dioxide is intimately mixed with the pulp in mixer 59 and discharged to retention vessel 61 via conduit 60. The alkaline and chlorinated pulp is

retained in conventional retention vessel 61 (e.g. an upflow vessel) for at least 1 hour, typically the pulp is retained for between about 1.5 to 6 hours, preferably between about 2 to 4 hours, at a temperature of between about 20 and 70°C, preferably, between about 50 and 70°C. The treated pulp is discharged via conduit 140 to conventional washer 141, washed, and then forwarded on to further treatment, as discussed previously, via conduit 142.

FIGURE 3 shows plots of three different treatment scenarios, a D-E<sub>op</sub>-(ZEND) treatment sequence according to the present invention indicated by reference numeral 70, and two prior art procedures, D-E<sub>op</sub>-D-P indicated at 71, and D-E<sub>op</sub>-D indicated at 72. It will be seen that the treatment 70 according to the present invention achieves brightness comparable to that of the procedure 71, yet with viscosity that is much higher, and in fact comparable to that indicated at 72. In all of the procedures 70, 71, 72 illustrated in FIGURE 3, the feed pulp before the treatment sequence was LO-SOLIDS® cooked mixed hardwood that was oxygen delignified to a kappa number of 9, exactly the same feed pulp being used for each of the treatments 70, 71, 72.

FIGURE 4 is a graph of the same pulps and treatment sequences as in FIGURE 3, only showing brightness graphed against chlorine dioxide consumption. Again as can be seen the treatment procedure 73 according to the present invention had brightness comparable to that of the procedure 74, and much greater than the procedure 75, with approximately the same (only slightly greater) chlorine dioxide consumption.

As clear from FIGURES 3 and 4, the treatment sequence D-E [typically either E<sub>0</sub>, or E<sub>p</sub>, or E<sub>op</sub>] – (ZEND) according to the invention produces pulp having a brightness of at least 89 or 90% ISO, and a viscosity of at least about 21 or 22 cP.

The invention includes all specific narrower ranges within the broad ranges recited above. For example, a consistency of 6-18% means 6-12%, 8-11%, 9-18%, and all other narrow ranges within the broad range.

Thus, according to the present invention, an environmentally-friendly and commercially-viable process for producing fully-bleached cellulose pulp from comminuted cellulosic fibrous material is provided. While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed

